PB85-237865

# Hazardous Waste Incineration in Industrial Processes Cement and Lime Kilns

(U.S.) Environmental Protection Agency
Cincinnati, OH

Jul 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-237865

EPA/600/D-85/146
July 1985

# HAZARDOUS WASTE INCINERATION IN INDUSTRIAL PROCESSES: CEMENT AND LIME KILNS

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SPRINGFIELD, VA. 22161

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## ABSTRACT

With more liquid wastes due to be banned from land disposal facilities, expanding hazardous waste incineration capacity becomes increasingly important. At the same time, industrial plants are increasingly seeking to find new sources of lower cost fuel, specifically from the disposal of hazardous wastes with heating value.

The Hazardous Waste Engineering Research Laboratory (HWERL) is currently evaluating the disposal of hazardous wastes in a wide range of industrial processes. The effort includes sampling stack emissions at cement, lime and aggregate plants, asphalt plants and blast furnaces, which use waste as a supplemental fuel. This reserach program is an essential part of EPA's determination of the overall environmental impact of various disposal options available to industry. This paper summarizes the results of the HWERL program of monitoring emissions from cement and lime kilns burning hazardous wastes as fuel.

## INTRODUCTION

With the passage of the Hazardous and Solid Waste Disposal Act of 1984, more categories of liquid hazardous wastes will be banned from land disposal facilities. At the same time, energy intensive industries are increasingly seeking to find new sources of less expensive fuel. Because many industrial waste products can be readily used as fuels and some hazardous wastes can be economically be processed and made into fuels, a market based on hazardous wastes has been developing in the U.S. [1], [2]. If reprocessed waste liquids do not contain significant quantities of toxic metals, halogenated materials, and PCBs, and have a high heating value, they can be economically substituted for coal, coke, oil or natural gas in many industrial processes. There are many examples of high temperature industrial furnaces and processes which already burn hazardous waste as supplemental fuel: cement kilns (both wet and dry proceses), lime and dolomite kilns, clay processing kilns, steel blast furnaces, phosphate rock calciners and dryers, iron ore dryers, brick and tile tunnel kilns, mineral wool furnaces and glass melt furnaces.

In particular, there has been a great deal of interest in the use of cement kilns for the disposal of industrial wastes as supplemental fuel for several reasons: 1) the production process is highly energy intensive; fuel savings may translate into a competitive advantage; 2) kiln temperatures are higher (2700°F) and gas residence times are longer (6-10 seconds) than those encountered in most hazardous waste incinerators; 3) cement product quality is relatively insensitive to addition of most waste trace impurities.

The Alternative Technologies Division of EPA's Hazardous Waste Engineering Research Laboratory-Cincinnati has been investigating hazardous waste incineration in cement kilns since 1977. A number of test programs on waste incineration by other organizations at cement plants have been conducted since 1974 in Canada, the U.S., and Western Europe and are listed in Table I.

The purpose of the tests, both in the U.S. and abroad, was to determine the effectiveness of the process in destroying hazardous wastes, while providing significant heat input into the process. The primary objectives of the test program were to document the performance of each facility and compare it to performance standards promulgated for incinerators. Secondary objectives were to document any changes in conventional pollutant emissions that could be attributed to burning hazardous waste and identify new problems.

This paper summarizes the data from these tests on: waste destruction and removal efficiency (DRE), hydrogen chloride (HCl) emissions, and changes in conventional pollutant emissions from kilns when burning hazardous wastes as supplemental fuel. From the RCRA standpoint, most important of these concerns are particulate matter, (DRE), and HCl results. Carbon monoxide, $NO_x$, total hydocarbons (THC), and $SO_x$ will also be discussed. For reference, a generalized diagram of a cement kiln burning waste as a fuel is shown in Figure 1.

TABLE I. SUMMARY OF CEMENT AND LIME KILN TESTS

| | Plant | Date | Process | APCD | Fuel | Wastes |
|---|---|---|---|---|---|---|
| 1. | St. Lawrence Cement<br>Mississauga, ON<br>[3,4] | 1974<br>1975-76 | Dry<br>Wet | ESP<br>ESP | Fuel oil<br>Fuel oil | Waste oil<br>Chlorinated organics |
| 2. | Stora Vika<br>Sweden [5,6] | 1978 | Wet | ESP | Coal | Chlorinated organics, PCB's, Freon 113 |
| 3. | Marquette Cement<br>Oglesby, IL [7] | 1981 | Dry | ESP | Coal | Hydrocarbon solvents (<5% chlorine) |
| 4. | San Juan Cement<br>Puerto Rico [8] | 1981-82 | Dry | ESP | Coal | Chlorinated organics |
| 5. | Alpha Cement<br>Cementon, NY [19] | 1982 | Wet | ESP | Coal | Solvents |
| 6. | General Portland<br>Lebec, CA [10] | 1982 | Dry | Baghouse | Coal | Hydrocarbon solvents |
| 7. | General Portland<br>Paulding, OH [11] | 1983 | Wet | ESP | Coal | Hydrocarbon solvents Freon 113 |
| 8. | Lone Star Industries<br>Oglesby, IL [12] | 1983 | Dry | ESP | Coal/Coke | Hydrocarbon solvents Freon 113 |
| 9. | Rockwell Lime<br>Manitowoc, WI [9] | 1983 | Lime | Baghouse | Coke | Hydrocarbon solvents |

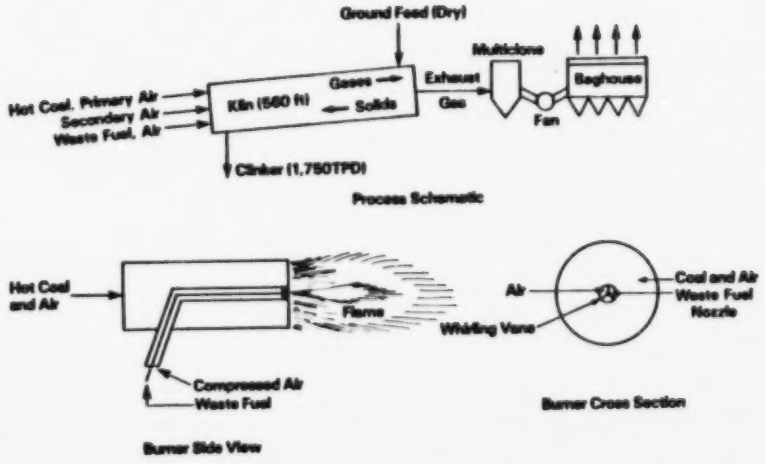



Figure 1. Generalized Diagram of a Cement Kiln Burning Hazardous Waste as Fuel

## PARTICULATE MATTER

Most of the tests conducted at kilns using electrostatic precipitators exhibited small or little change in particulate emissions when burning hazardous wastes. A summary of the average data for each test is listed in Table II. The major exceptions are tests during which there were either process equipment malfunctions [4, 12] or high amounts of chlorine being fed to the kiln (4, 5, 6). The latter tests have led to the conclusion that the higher chlorine input to the kiln will lead to greater particulate emissions.

In a review article, Weitzman [14] discussed particulate emissions from cement kilns burning chlorinated wastes as fuel. Data from the St. Lawrence Cement and Stora Vika tests were re-examined, compared, and were plotted as a function of chlorine feed rate. The resulting graph showed a linear increase in particulate emissions as a function of chlorine input to the process. In the article, he hypothesized that the hydrogen chloride combustion product reacts with the potassium, sodium, and calcium compounds in the hot kiln to form the respective chlorides and the volatilized chloride salts were carried by the hot gas to the cooler end of the kiln where they condensed at about 800°C to form a fine particulate. The higher chloride content of the particulate, with concomitant changes in dust resistivity, lowered the electrostatic precipitator (ESP) collection efficiency. This resulted in significantly increased dust emissions during the two chlorinated organic waste firing tests. Based on the results of these tests and the hypothesis of very fine particles, Weitzman concluded that a kiln using a fabric filter for particulate removal would encounter a similar deterioration in efficiency.

The particulate emissions from the kiln tested at San Juan Cement[8], equipped with a fabric filter dust collecting system, did not exhibit an increase with progressively larger chlorine input as shown in Figure 2. For comparison, the linear regression plot developed from the St. Lawrence Cement and Stora Vika data are also displayed. It can be seen that, not only was more organic chlorine fed to the kiln at San Juan Cement than more of the previous tests, the fabric filter system was able to maintain a high collection efficiency regardless of the amount of chlorine fed to the kiln.

Thus, the addition of substantial amounts of organic chlorine in waste fuel may contribute to lowering ESP collection efficiency, but has no effect on control efficiency of fabric filters. [15]

## DESTRUCTION AND REMOVAL EFFICIENCIES FOR PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS

Incinerators and, in the near future, other facilities burning hazardous wastes, must perform at a minimum to the standards described in the Federal regulations [22]. Specifically, with regard to the Principal Organic Hazardous Constituents (POHC's), the facility must achieve a destruction and removal efficiency (DRE) of 99.99% for each designated POHC. The DRE is determined as follows [22]:

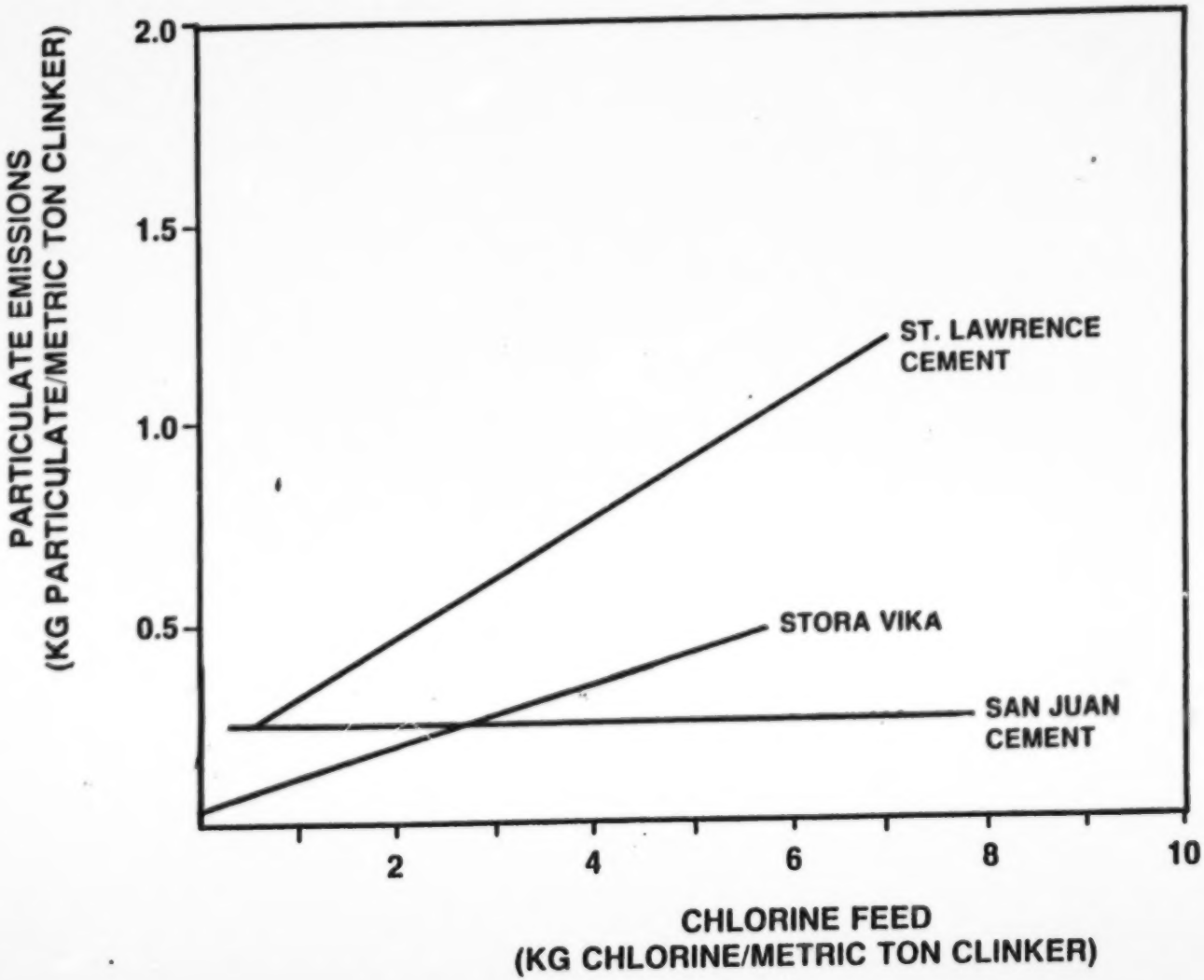



Figure 2. Illustration of variations in Particulate Emmisions with chlorine in kiln feed

TABLE II. SUMMARY OF PARTICULATE EMISSION DATA

| Plant | Test Condition | Particulate Emissions | | | Chloride Input to Kiln |
|---|---|---|---|---|---|
| | | gs/scf | lb/hr | lb/ton | (kg/Mg) |
| St. Lawrence | Chlorinated aliphatics[1] | 0.21 | 123 | 3 | 4.0 |
| | Chlorinated aromatics | 0.286 | 45 | 1.1 | 5.5 |
| | PCB's | 0.078 | 44 | 1.1 | 2.5 |
| | Baseline | 0.038 | 21 | 0.5 | - |
| | Lubricating oil | 0.064 | 83 | 0.7 | - |
| | Baseline | 0.107 | 139 | 1.1 | - |
| Rockwell Lime | Waste | 0.016 | 2.2 | 0.26 | 2.7 |
| | Baseline | 0.013 | 2.0 | 0.24 | - |
| Stora Vika | Aliphatics | 0.039 | 21 | 0.88 | 4.4 |
| | Baseline | 0.009 | 4.7 | 0.21 | 0 |
| | PCB's | 0.024 | 12.7 | 0.53 | 3.6 |
| | Baseline | 0.011 | 5.9 | 0.25 | 0 |
| | Chloraphenols and Phenoxyacids | 0.058 | 30.9 | 1.36 | 0.95 |
| | Baseline | 0.014 | 7.7 | 0.34 | 0 |
| | Freon 113 | 0.062 | 33.3 | 1.39 | 1.7 |
| | Baseline | 0.022 | 11.7 | 0.49 | 0 |
| Marquette | Waste solvents | 0.014 | 58 | 21 | 1.1 |
| | Baseline | 0.093 | 80 | 20.8 | - |
| Alpha Cement | Solvents | 0.041 | 44 | 0.8 | - |
| | Baseline | 0.050 | 53 | 1.1 | - |
| San Juan | Wastes | 0.043 | 22.4 | 0.66 | 5.5 |
| | Baseline | 0.041 | 21.7 | 0.64 | - |
| General Portland Paulding | Wastes | 0.030 | 18.9 | 0.65 | 2.2 |
| | Baseline | 0.030 | 19.6 | 0.64 | 0.2 |
| Lone Star | Waste[2] | | | | 1.2 |
| | Baseline | 0.17 | 116 | 2.0 | 0.2 |

1 Process upset during test
2 ESP malfunctioned during test

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

where: $W_{in}$ = mass feed rate of a specific POHC in waste feed stream.

$W_{out}$ = mass flow rate of the same POHC in exhaust emissions to the atmosphere.

Table III summarizes the results of the tests which revealed reliable DRE data.

One of the first tests to examine the DRE of hazardous waste in cement kilns was conducted at a Canadian plant, St. Lawrence Cement. The wet-process kiln was normally fired with fuel oil and the exhaust gas was cleaned by an ESP. Three tests were conducted with batches of waste solvents labeled as chlorinated aliphatics, chlorinated aromatics, and PCBs. The chlorinated aliphatics were composed primarily of chloropropane, chloropropene, 1,2-dichloroethane, 1,1,2-trichloroethane, and chlorobenzene. The chlorinated aromatics batch was primarily chlorotoluene, and the waste labeled PCBs was about 50 percent PCB, 28.5 percent chlorotoluene, and a mixture of chlorinated aliphatics. Destruction efficiencies were calculated conservatively by not subtracting or correcting for the background levels from the baseline test or interferences (contamination) on the control blanks. In addition, a conservative collection efficiency of 80 percent was used. The result was a maximum estimated concentration of 50 ppb for all of the waste fuel tests, and "because of the high and uncertain background levels, the estimate of emissions is higher than the actual levels in the emissions"[4]. The DREs were calculated on total chlorinated organics basis rather than on the actual analysis of specific compounds. The reported DREs for wastes with mostly chlorinated organics was >99.99 pecent, >99.989 percent for chlorinated aromatics, and >99.986 percent for PCB mixtures [4].

A test similar to the one conducted at St. Lawrence was conducted in Sweden at a wet process kiln in Stora Vika. Short-term tests were conducted with chlorinated aliphatics (100 hr), PCBs (24 hr), chlorophenols and phenoxy acids (12 hr) and trichlorotrifluoroethane (Freon 113) (3 hr). Long-term tests were conducted with the chlorinated organics (1.5 months) and PCBs (about 1 month).

Results are listed in Table III. During both the short- and long-term tests with chlorinated aliphatics, none of the waste fuel's major components were detected in the stack gas. Based on the detection limit, the DRE of methylene chloride exceeded 99.995 percent and the DRE of trichloroethylene exceeded 99.9998 percent [5], [6].

No PCBs were detected in the stack gas during either the short- or long-term test and yielded a DRE exceeding 99.99998 percent for PCB. Similarly, no chlorophenols or phenoy acids were detected in the stack gas; DREs were calculated to be greater than 99.99999 and 99.99998 percent, respectively. Detectable

TABLE III. SUMMARY OF DRE DATA

| Plant | Waste Component | Destruction Efficiency |
|---|---|---|
| St. Lawrence Cement | Chlorinated aliphatics | >99.990 |
| | Chlorinated aromatics | >99.989 |
| | PCB's | >99.986 |
| Stora Vika | Methylene chloride | >99.995 |
| | Trichloroethylene | >99.9998 |
| | All chlorinated hydrocarbons | >99.988 |
| | PCB | >99.99998 |
| | Chlorinated phenols | >99.99999 |
| | Phenoxy acids | >99.99998 |
| | Freon 113 | >99.99986 |
| San Juan Cement | Methylene chloride | 93.292-99.997 |
| | Trichloromethane | 92.171-99.96 |
| | Carbon tetrachloride | 91.043-99.996 |
| Los Robles (General Portland) | Methylene chloride | >99.99 |
| | 1,1,1-Trichloroethane | 99.99 |
| | 1,3,5-Trimethylbenzene | >99.95 |
| | Xylene | >99.99 |
| Paulding (General Portland) | Methylene chloride | 99.956-99.998 |
| | Freon 113 | >99.999 |
| | Methyl ethyl ketone | 99.978-99.997 |
| | 1,1,1-Trichloroethane | 99.991-99.999 |
| | Toluene | 99.940-99.988 |
| Oglesby (Lone Star) | Methylene chloride | 99.94-99.99 |
| | Freon 113 | 99.999 |
| | Methyl ethyl ketone | 99.997-99.999 |
| | 1,1,1-Trichloroethane | >99.999 |
| | Toluene | 99.986-99.998 |
| Rockwell Lime | Methylene chloride | 99.9947-99.9995 |
| | Methyl ethyl ketone | 99.9992-99.9997 |
| | 1,1,1-Trichloroethane | 99.9955-99.9982 |
| | Trichloroethylene | 99.997-99.9999 |
| | Tetrachloroethylene | 99.997-99.9999 |
| | Toluene | 99.995-99.998 |

levels of were Freon 113 were found during one experiment with this waste fuel and yielded a DRE of 99.99986 percent [5], [6].

The test at the General Portland's Los Robles dry process kiln included dichloromethane, 1,1,1-trichloroethane, 1,3,5-trimethylbenzene, and xylene as POHC's in the waste fuel. The results show a DRE of 99.99 percent or greater for 3 of the 4 compounds and again, the calculations are conservative. No corrections were made for baseline levels or for the contribution from ambient air. No trimethylbenzene was detected; therefore, the DRE for this compound is likely to have exceeded 99.95 percent [10].

In the tests at General Portland's Paulding, Ohio plant, DRE's for the most part were greater than 99.99 percent and in some cases higher than 99.999 percent. DRE's less than 99.99 percent for methyl ethyl ketone and methylene chloride were related to sample contamination problems and do not represent poor incineration performance of the kiln. No problems with contaminants were seen with the 1,1,1-trichloroethane and Freon 113 results, which demonstrated DRE's of 99.999 percent or greater.

The results of the test burn at Lone Star showed similar contamination problems with methylene chloride. However, the DRE's for other compounds were all greater than 99.99 percent on conservative basis; i.e., no correction for blanks. In addition to the POHC's, several other compounds were tracked for DRE. Styrene, ethyl benzene, orthoxylene, and benzaldehyde all showed DRE's greater than 99.998%, which indicates that excellent destruction conditions existed in the kiln [15].

Waste fuel containing methylene chloride, methyl ethyl ketone, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and toluene was burned during the test at Rockwell Lime. The average DRE results are listed in Table III and show an average of 99.99 percent or greater. The reported DREs are again conservative because no blank corrections were applied. DREs exceeding 99.99 percent were consistently obtained for all POHCs.

The test at San Juan used methylene chloride, chloroform, and carbon tetrachloride as the designated POHCs in a waste fuel with very high chlorine contents (6.5-35.1 percent). This test showed a phenomenon seen at other cement kiln tests: measurable emission rates of the POHCs during the baseline test when no waste was burned. Blank samples showed no contamination problems; therefore, the source of the POHCs during the baseline was unexplainable. The reported DREs for this test (Table III) are low compared with other test results. The test report concluded that lack of air atomization of the waste fuel and the difficulty of incinerating highly chlorinated monocarbon compounds contributed to the low DREs. Above normal free lime content of the clinker product and removal of chloride in the clinker instead of the waste dust also suggest that operating difficulties were experienced in the kiln. However, the detection of POHCs during the baseline make the DRE results difficult to interpret. If the measured POHCs originated from sources other than burning waste fuel, the actual DREs may have been higher than those measured [8].

TABLE IV. SUMMARY OF THE THC AND CO CONCENTRATIONS

| Site | Test condition | THC (ppm)[a] | CO (ppm) |
|---|---|---|---|
| San Juan | Waste burn | 12.7 | 24 - 738[b] |
| | Baseline | 8.3 | 25 - 349[b] |
| Los Robles | Waste burn | [c] | 25 - 100 |
| General Portland | Baseline | 4 | 10 - 618 |
| Paulding | Waste burn | 21 | 190 |
| General Portland | Baseline | 10 | 212 |
| Lone Star | Waste burn | 5 | 24 - 49[b] |
| | Baseline | 2.5 | 35 - 40[b] |
| Rockwell Lime | Waste burn | 3.5 | 599 |
| | Baseline | 8.2 | 477 |
| Stora Vika | Chlorinated aliphatics | <10 | 300 - 1500 |
| | Baseline | <10 | 1,500 |
| | PCBs | <10 | 100 - 1500 |
| | Baseline | <10 | 100 |
| | Chlorophenols/phenoxy acids | 10 | 50 - 500 |
| | Baseline | 10 | 50 |
| | Freon | <10 | 100 - 500 |
| | Baseline | <10 | 100 |

[a] Expressed as ppm methane unless otherwise noted.

[b] Range of test averages.

[c] Not measured.

The San Juan test, when viewed with results from other cement kiln tests, suggests that burner design, waste composition, and the kiln's operation can have a significant effect on DRE performance. The extent of their effect is inconclusive because of baseline POHC emissions.

## CARBON MONOXIDE AND TOTAL HYDROCARBONS

CO emissions are not affected by the burning of waste fuels. Weitzman noted that changes in CO can be indicative of flame quenching, improper burner adjustment, or other imbalances in the flame [14]. Peters and Mournighan [15] found that any process change can create a significant CO excursion. Examples of process changes include alternation of: the primary air/fuel ratio, secondary air flow, solid fuel feed rates, and product cooler exhaust flow. These effects were observed during the Paulding test during a kiln upset with coal as the only fuel. Over the course of the event, several process parameters were changed and large swings in CO concentrations (as well as other monitored gas concentrations) were observed. The CO results for Stora Vika also show a wide range of 50-1500 ppm for both the baseline and waste fuel burns. Table IV lists CO and total hydrocarbons for each of the tests.

The CO results for Lone Star appear to be the most consistently low. The kiln was operated with a higher $O_2$ input (to aid in drying wet coal), which apparently resulted in very consistently low levels of THC, CO and $SO_2$ with increased $NO_x$ concentrations. The Los Robles kiln was also very stable during three waste firing tests in which the maximum CO was 100 ppm.

The CO results indicate that the feeding of waste fuel to the kiln does not significantly affect CO concentrations. Process stability apparently has a greater effect on CO concentrations. CO monitors on kilns provide the operator with a measure of this stability. The CO measuring equipment in general use by the industry is not as sensitive as the equipment used by the test crews and is not capable of seeing CO concentrations much below 1000 ppm. Installation of more sensitive CO monitors would help operators control combustion conditions more effectively.

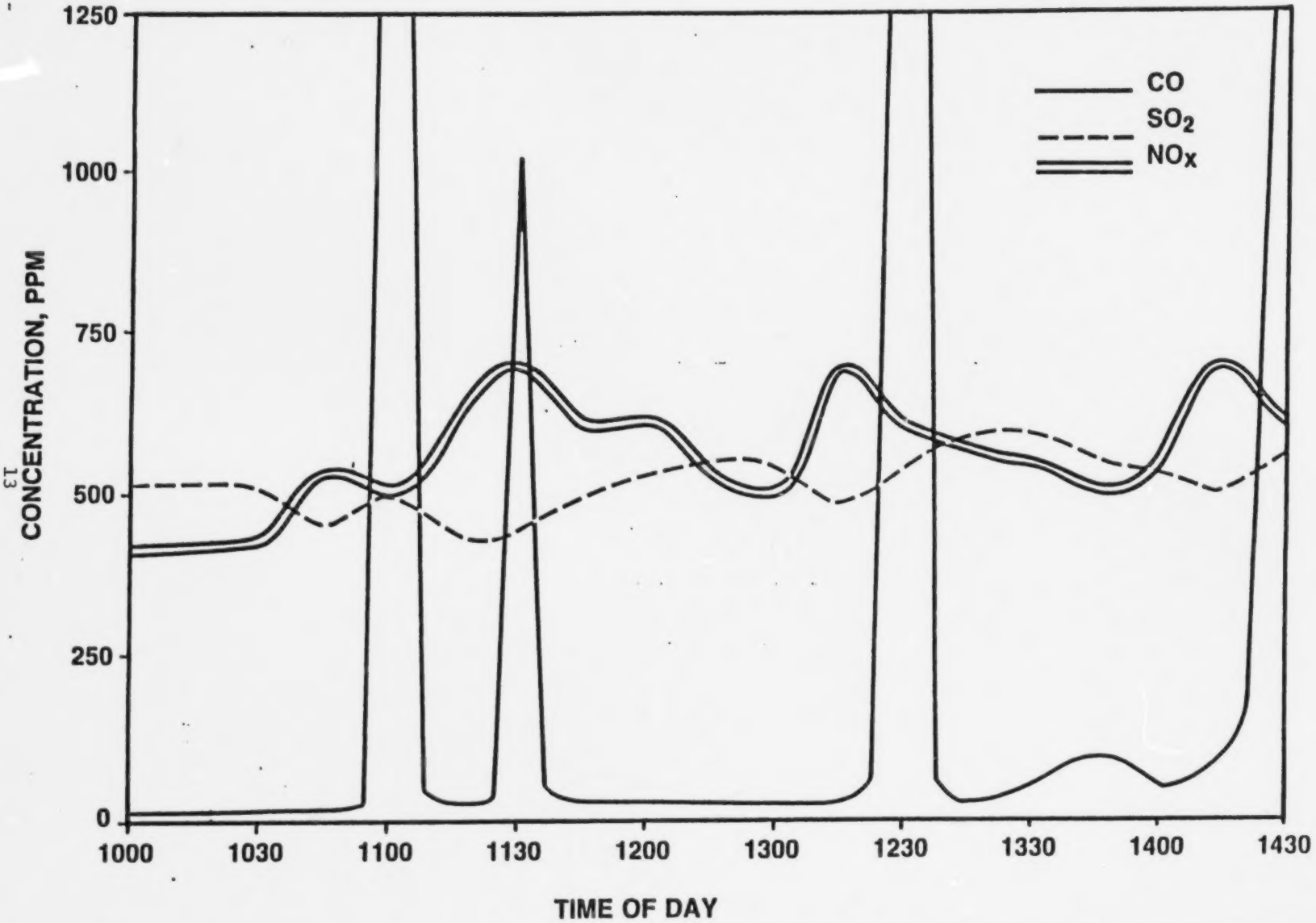
Total hydrocarbons (THC) increased during waste fuel combustion at 3 tests, decreased at 2 tests, and remained the same at another. The consistently low THC concentrations for several different types of compounds at Stora Vika suggest that kiln operation may affect THC concentrations more than the waste type does. The levels at Rockwell Lime, which attained consistently high DRE's, averaged 3.5 ppm. Similarly, the Lone Star kiln maintained consistently low levels of the THC between 2.5 and 5 ppm. These data for different types of kilns and wastes fuels indicate that a well-controlled kiln can operate with average THC concentrations below 10 ppm.

## NITROGEN OXIDES

In cement and limes kilns, there is a direct functional relationship between $NO_x$ emissions and secondary combustion air flow and temperature. There is usually little or no $NO_x$ formed from nitrogen in fuel relative to $NO_x$ from combustion air. Kilns are generally operated as "poor" combustors. When compared to boilers and incinerators, kilns have a reduced primary air/fuel mix, poorer secondary air mixing, and often require a confined, narrow flame configuration for good product quality. Typical $NO_x$ concentrations in the stack gas can range from 200 to 1500 ppm, depending on combustion conditions. $NO_x$ levels are very operator-dependent; continuous monitoring has shown that at some kilns $NO_x$ levels vary widely from hour to hour, while others can maintain steady $NO_x$ concentrations for days at a time. These and other tests conducted under the USEPA $NO_x$ Reduction Program [20] tests indicate that waste firing has little to do with $NO_x$ variations. The amount of excess air, secondary air temperature, and primary air/fuel ratios are the main determinants in kiln $NO_x$ emissions [15].

Table V present a summary of the tests for which $NO_x$ emissions data is available. At both Marquette Cement and San Juan Cement a significant decrease was observed during waste firing. This may have been the result of lowered oxygen input more than waste firing. At the General Portland - Los Robles Plant, the $NO_x$ emissions decreased slightly the change was not statistically significant. A significant increase was observed at Rockwell Lime, but the change was intended so that the $NO_x$ emissions increased during waste firing.

A definite relationship between $O_2$, $NO_x$, and $SO_2$ in calcination kilns has been shown [20]. $NO_x$ emissions decrease with decreasing $O_2$ input and lower secondary air temperatures, while $SO_2$ emissions increase. For instance, a 38% reduction in $NO_x$ due to $O_2$ lowering can cause a 47% increase in $SO_2$. Continuous monitoring at Rockwell Lime and General Portland-Paulding illustrated that $NO_x$ and $SO_2$ change inversely, as shown in Figure 3. Moreover, the $NO_x/SO_2$ change is followed within 5-15 minutes by a CO spike, the kiln's indicator of a momentary process instability. As shown in Figure 3, this event recurred at uneven intervals.




Figiure 3. Illustration of interrelationships between $NO_x$, $SO_2$, and CO Emissions in a Lime Kiln

TABLE V. SUMMARY OF $NO_x$ EMISSIONS DATA

| Test | Condition | $NO_x$ (lb/hr) | $NO_x$ (lb/ton) | (ppm) | Comments |
|---|---|---|---|---|---|
| Marquette | Waste | 275 | 4.6 | 544 | Significant decrease in $NO_x$ |
| | Baseline | 404 | 6.7 | 920 | |
| San Juan | Waste | 31.3 | 0.9 | 68 | Significant decrease in $NO_x$ |
| | Baseline | 60.4 | 1.8 | 136 | |
| Los Robles | Waste | 304 | 5.3 | 486 | No significant decrease in $NO_x$ [15] |
| | Baseline | 444 | 8.2 | 680 | |
| Paulding | Waste | 174 | 6.0 | 478 | Significant increase in $NO_x$ |
| | Baseline | 140 | 4.6 | 371 | |
| Lone Star | Waste | 472 | 8.6 | 814 | Significant increase in $No_x$ |
| | Baseline | 371 | 6.9 | 620 | |
| Rockwell Lime | Waste | - | - | 446 | Significant increase in $NO_x$ |
| | Baseline | 134 | 15.8 | 386 | |

## ACID GASES

The process materials in cement kilns, by their alkaline nature, provide built-in control for acid gases such as $SO_2$ and HCl. In a well operated cement kiln with medium-to high feed alkalinity, $SO_2$ will be scrubbed in the kiln environment and be adsorbed by the alkaline dust of the air pollution control device to control efficiencies of greater than 90%. For HCl emissions, a removal of efficiency greater than 99% was observed at San Juan Cement, where high amounts of chlorine were added to a kiln processing relatively low alkaline materials [8]. Tables VI and VII present the emission results for $SO_2$ and HCl, respectively, for all tests.

As shown in Table VII, HCl results are quite variable from test to test. For the most part, however, HCl emissions are low and less that the standard set for incinerators [21]. Notable exceptions are the Marquette and Lone Star tests. The results of the Lone Star tests are suspect because of ESP malfunction.

Waste fuels typically do not contain much sulfur and thus the partial substitution of waste fuel for fuel oil or coal will reduce sulfur input to the kiln, resulting in less $SO_2$ to being formed. During the Marquette Cement test, where a 13% energy substitution was fired, $SO_2$ stack gas concentrations were reduced from 93 ppm to 18 ppm. At the Los Robles cement plant, no significant difference in $SO_2$ emissions was noted. $SO_2$ emissions increased significantly at San Juan Cement, from 280 ppm to 450 ppm, probably for two reasons: the $NO_x$ emissions were reduced--indicative of lower $O_2$ input-- and the high rate of chlorine input may have caused a competitive acid gas "scrubbing" situation-HCl was preferentially absorbed over $SO_2$. The kiln operator's choice of $O_2$ input will have a greater effect on $SO_2$ emissions than addition of a waste fuel. The test results indicate that it is possible, and probably preferable to operate a cement kiln with less than 50 ppm $SO_2$ in the stack gas, when burning hazardous waste.

At Rockwell Lime, however, a different mode of operation was required; $SO_2$ is not intentionally absorbed because the presence of sulfur in their lime product is undesirable. No significant difference was observed for $SO_2$ emissions, which remained between 500-600 ppm regardless of waste firing.

The data indicate that effects of chlorinated waste combustion on HCl emissions are quite variable from kiln to kiln. Variations in HCl emissions with time can also exist within the same kiln, depending on operating conditions. Sporadic variations in HCl can be expected because of cyclic temperature variations, feed and fuel changes that affect the kiln temperature profile, and chloride loading, and variations in recycle dust rate and composition.

The continuous monitoring of $SO_2$, $NO_x$, $O_2$ and CO indicated that the concentration of these compounds in the stack gas are interdependent and combustion operation can be optimized. Use of continuous monitors proved to be an excellent

TABLE VI. SUMMARY OF $SO_2$ EMISSION DATA

| Test | Condition | $SO_2$ Emissions (lb/hr) | (lb/ton) | (ppm) | Comments |
|---|---|---|---|---|---|
| Alpha Cement [19] | Waste | 58.5 | 1.1 | 33 | S in coal = 2.6%; S in waste = 0.2% |
| | Baseline | 138 | 2.7 | 78 | S during waste burn = 2.0% |
| Marquette | Waste | 11.5 | 0.19 | 18 | S in waste = 0.08% |
| | Baseline | 57.1 | 0.95 | 93 | Significant decrease |
| San Juan | Waste | 264 | 8 | 450 | S in fuel oil = 2.15% |
| | Baseline | 170 | 5 | 279 | Significant increase |
| Los Robles General Portland | Waste | 21.7 | 0.36 | 27 | S in coal = 0.43% |
| | Baseline | 23.7 | 0.38 | 27 | No significant difference |
| Paulding General Portland | Waste | 297 | 6.8 | 265 | S in coal = 4.3% |
| | Baseline | 526 | 17.2 | 636 | Significant decrease |
| Lone Star | Waste | 6.7 | .12 | 19 | S in coal/coke = 2.7% |
| | Baseline | 5.6 | .10 | 7 | Significant increase, but very low |
| Rockwell Lime | Waste | 97 | 11.4 | 596 | S in coke = 4.15 |
| | Baseline | 149 | 17.5 | 553 | No significant difference |

TABLE VII. SUMMARY OF HCl EMISSION DATA

| Test | Condition | HCl Emissions (lb/hr) | (lb/ton) |
|---|---|---|---|
| Alpha Cement [19] | Waste | 5.8 | 0.11 |
| | Baseline | 2.4 | 0.05 |
| Marquette | Waste | 115 | 1.9 |
| | Baseline | 190 | 3.2 |
| San Juan | Waste | 0.79 | 0.02 |
| | Baseline | 0.19 | 0.006 |
| Los Robles (General Portland) | Waste | 1.03 | 0.015 |
| | Baseline | 0.55 | 0.007 |
| Paulding (General Portland) | Waste | 4.62 | 0.16 |
| | Baseline | 1.25 | 0.04 |
| Lone Star | Waste | 25.3 | 0.46 |
| | Baseline | 2.9 | 0.054 |
| St. Lawrence | Waste | 1 | 0.02 |
| | Baseline | 1 | 0.02 |
| Rockwell Lime | Waste | 0.44 | 0.05 |
| | Baseline | 0.20 | 0.02 |

process monitoring tool because of the increased information feedback on combustion conditions. Although continuous monitoring equipment requires constant attention and maintenance, their worth as a process control tool may prove quite valuable.

## CONCLUSIONS

The foregoing examples of burning liquid hazardous wastes as a fuel supplement in cement and lime kilns in Canada, Sweden, Illinois, Puerto Rico, California, and Wisconsin have demonstrated that there is little or no significant change in emissions of conventional pollutants and that process operation changes have a greater effect on changes in emissions than the partial substitution of hazardous waste fuel.

The conventional pollutants which show little or no significant change and are independent of hazardous-waste-as-fuel burning are CO, THC, $NO_x$ and $SO_2$. Previous studies and evaluation of continuous monitoring demonstrated that emissions rates of these compounds are more a function of combustion air flows and fuel rate control than any of the other parameters.

Particulate emissions from kilns equipped with electrostatic precipitators may be expected to increase with increasing chlorine loading in the kiln. Those kilns equipped with fabric filters, or baghouses, will not experience any significant change in emissions.

HCl emissions from cement and lime kilns meet emission limits set for incinerators. However, variations in test results warrant further investigation into this issue.

Destruction and Removal Efficiencies (DRE) of POHC's were, for the most part, greater than the incinerator regulatory requirement of 99.99%. It appears that there are enough variations in kiln operation from plant to plant, that variations in DRE would be expected, but a well operated facility should have little trouble in demonstrating compliance with the DRE requirement.

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**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA/600/D-85/146 | | PB85 237865/AS |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| HAZARDOUS WASTE INCINERATION IN INDUSTRIAL PROCESSES: Cement and Lime Kilns | July 1985 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) Mournighan,RE ,Peters JA, Branscome MR, & Freeman HM | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Hazardous Waste Engineering Research Laboratory<br>Office of Research And Development<br>U.S. Environmental Protection Agency<br>Cincinnati, OH 45268 | 10. PROGRAM ELEMENT NO. |
| | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Hazardous Waste Engineering Research Laboratory<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Cincinnati,OH 45268 | 13. TYPE OF REPORT AND PERIOD COVERED |
| | 14. SPONSORING AGENCY CODE<br>EPA/600/12 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

With more liquid wastes due to be banned from land disposal facilities, expanding hazardous waste incineration capacity becomes increasingly important. At the same time, industrial plants are increasingly seeking to find new sources of lower cost fuel, specifically from the disposal of hazardous wastes with heating value.

The Hazardous Waste Engineering Research Laboratory (HWERL) is currently evaluating the disposal of hazardous wastes in a wide range of industrial processes. The effort includes sampling stack emissions at cement, lime and aggregate plants, asphalt plants and blast furnaces, which use waste as a supplemental fuel. This reserach program is an essential part of EPA's determination of the overall environmental impact of various disposal options available to industry. This paper summarizes the results of the HWERL program of monitoring emissions from cement and lime kilns burning hazardous wastes as fuel.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 25 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | UNCLASSIFIED | |

EPA Form 2220-1 (9-73)